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(21) International Application Number: PCT/US90/00973 (22) International Filing Date: 20 February 1990 (20.02.90) (30) Priority data: 313,371 21 February 1989 (21.02.89) US (71) Applicant: UNION OIL COMPANY OF CALIFORNIA [US/US]; P.O. Box 76, 376 South Valencia Avenue, Brea, CA 92621 (US). (72) Inventors: CROUDACE, Michael, C. ; 13811 Glenmere Drive, Santa Ana, CA 92705 (US). WESSLER, Gerald, A. ; 17197 Santa Barbara, Fountain Valley, CA 92708 (US).		(74) Agent: HACKLER, Walter, A.; 2302 Martin Street, Suite 320, Irvine, CA 92715 (US). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (Eu- ropean patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FUEL COMPOSITION FOR CONTROL OF INTAKE VALVE DEPOSITS (57) Abstract A motor fuel composition comprising (1) a gasoline suitable for combustion in a spark-ignited internal combustion auto- motive engine, and (2) an intake valve deposit controlling amount of an additive comprising one or more C ₆ + aliphatic primary amines, one or more gasoline dispersants selected from the group consisting of polyalkylamines and Mannich bases, and a nonvolatile-fluidizer oil. <i>no proportions - optimize</i>		

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FUEL COMPOSITION FOR CONTROL OF INTAKE VALVE DEPOSITS

FIELD OF THE INVENTION

The present invention relates to improved hydrocarbon fuel compositions which control the formation and buildup of intake valve deposits in spark-ignition engines and more particularly to a deposit controlling additive composition for gasoline fuels used in said engines.

DESCRIPTION OF THE PRIOR ART

Recently, the automobile industry has had serious problems in the operation of high performance, multiport fuel injected engines tuned close to their lean burn combustion limits. Examination of these engines shows that the problem is a result of a buildup of deposits on the fuel intake valves. A failure to prevent such deposit buildup leads to impaired drivability. Even small amounts of these valve deposits result in rough idle, stalling, hesitation and surging, particularly during the cold start, warmup phases of the driving cycle.

This condition was first observed in Europe during the late 1970's and early 1980's, with several makes of cars being involved and commercial premium leaded gasolines being used. These gasolines were low in unsaturated hydrocarbons (typically 5-8%) and were not expected to generate troublesome deposits. However,

very thin deposits did develop on the intake valve tulip surfaces, and these were enough to cause starting/warmup drivability problems. This poor performance generally became apparent within 16,000 to 32,000 km of driving and resulted in many complaints under warranty by the owners. The general solution to this problem was to change gasoline additive treatments from conventional carburetor/port fuel injector detergents to polymeric dispersant formulations at three to ten times conventional detergent levels.

Some of the vehicle types exhibiting intake valve deposit problems in Europe exhibited the same problems when operated with at least some of the unleaded gasolines marketed in the United States. While the number of affected vehicles is, at present, not very large, it has been suggested by several observers that they exemplify a future trend toward lean-burn, high efficiency engines.

Most recently, BMW has proposed that the maximum limit of intake valve deposit buildup be 100 mg/10,000 miles of driving as established by a standard test procedure developed by them and run at the Southwest Research Institute. Gasolines passing this test are given a lifetime BMW approval. However, the amounts of intake valve deposit control detergents which must be used to meet this standard are often so high, that it is not economical in all grades of fuel. In still other cases, the gasoline detergent itself has been found to result in an increase in intake valve deposits.

Consequently, there is a need for motor fuels containing an additive composition to prevent or reduce the formation and buildup of intake valve deposits to levels below the BMW standard while keeping port fuel injectors clean at economic treatment levels.

SUMMARY OF THE INVENTION

It has now been found that a significant reduction in intake valve deposit formation and buildup is produced when an intake valve deposit control additive, comprised of a detergent selected from the group consisting of one or more C_6+ aliphatic primary amines, one or more gasoline dispersants selected from the group consisting of polyalkylamines and Mannich bases, and a nonvolatile fluidizer oil is added to gasoline. The amount of additive used in the fuel is typically in the range between about 50 and about 1000 PTB.

Accordingly, the invention provides a method for operating a spark-ignition internal combustion engine which comprises introducing with the fuel an intake valve deposit controlling amount of said intake valve deposit control additive.

The invention further provides a motor fuel composition comprising (1) a gasoline suitable for combustion in an automotive multiport fuel injected internal combustion engine, usually boiling in the gasoline range of about 100° F to about 437° F and (2) an intake

valve deposit controlling amount of said intake valve deposit control additive.

Further provided according to the present invention is an intake valve deposit controlling additive concentrate comprising (a) from about 50 to about 4000 grams per gallon of said additive and (b) the balance being a fuel-compatible diluent suitable for combustion in an automotive spark-ignition internal combustion engine.

When the additive is used in a typical premium grade unleaded gasoline, the compounded fuel produces a level of intake valve deposit formation and buildup which is well below both the level required for BMW lifetime certification and that exhibited by the fuel either by itself or with either additive component used alone.

DETAILED DESCRIPTION OF THE INVENTION

As used herein the term detergent denotes that class of chemical compounds compositions which reduce or prevent deposits in automobile spark-ignition internal combustion engines operated at high speeds and temperatures. A dispersant is defined as a type of detergent primarily adapted to the dispersion of deposit precursors formed during relatively low temperature operation of said engines. Detergents and dispersants are closely related in that both of them solubilize engine deposits. The term BMW Test refers to a test procedure as described by Bitting et al. in "Intake

Valve Deposits - Fuel Detergency Requirements Revisited" (SAE Paper 872117), the teaching of which is herein incorporated by reference, in its entirety.

The intake valve deposit control additive of the present invention comprises a mixture of a long chain primary amine carburetor detergent, a fuel dispersant, and a fluidizer oil. The long chain primary amines suitable for use in the present invention are those having the formula RNH_2 , in which R is a C_6+ , typically C_6 to C_{40} aliphatic radical, with R preferably being either (1) an alkyl or akenyl radical having from about 12 to about 22 carbon atoms or (2) a radical of the form $R-O-R'$ wherein R and R' are independently C_2 to C_{20} aliphatic radicals. It should also be noted that if R is chosen to be an alkenyl group, mono-olefins are preferred. The amine to be employed may be a single amine or may comprise mixtures of such amines.

A particularly effective, and preferred, amine is an 18 carbon atom, mono-unsaturated amine, oleyl amine, which is obtainable from the Armak Chemicals Division of Akzo America under the trade names Armeen O, Armeen OL or Armeen OD, the distilled form thereof, and from Sherex Chemical Co. as Adogen 172 or Adogen 172D.

Other suitable amines which are generally mixtures of aliphatic amines include Adogen 170, Adogen 170D, Armeen T and Armeen TD, the latter being the distilled form of Armeen T which contains a mixture of 0-2% of tetradecyl amine, 24% to 30% of hexadecyl amine, 25% to 28% of octadecyl amine, and 45% to 46% of octadecenyl

amine. Armeen T and TD and Adogen 170 and 170D are derived from tallow fatty acids and are usually termed "tallow amines."

Lauryl amine is also suitable, as is Adogen 163 or Armeen 12, or the distilled form Armeen 12D, also obtainable from the above named suppliers. Typically the distilled product comprises 0-2% of decyl amine, 0-3% of tetradecyl amine, 90% to 95% of dodecyl amine, 0-1% of octadecenyl amine.

In addition to the various amines described above, the mixture of amines derived from soya fatty acids also falls within the class of amines above described as suitable for use according to this invention. Whatever the source, those amines having about 16 to about 18 carbon atoms are most preferred, and oleyl amine is the most particularly preferred long chain amine for use in the present invention.

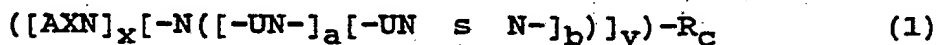
In addition to alkyl and alkenyl amines, "ether" amines of the form $R-O-R'-NH_2$ are also suitable for use as the detergent constituent of the present invention. Preferred for R and R' are aliphatic radicals, more preferred are hydrocarbyl radicals, with alkyl and alkenyl radicals being most preferred, said radicals independently ranging between about 2 and about 20 carbon atoms, with the combined total of carbon atoms in R and R' being between about 10 and about 30. More preferred are compounds where R ranges between 10 and 20, and R' ranges between 2 and 10 carbon atoms and, in the most preferred compounds, R is between 12 and 15

and the total number of carbon atoms in R and R' is between 15 and 20. One commercially available material conforming to this description are Adogen 185 which is a mixture of dodecyloxy to pentadecyloxy propyl amines. Others are Sherex MG 98, which is a mixture of octyloxy to decyloxy propyl amines, and MG 70, which is 1-methylnonyloxy propyl amine. In addition, the corresponding ethyl and butyl amines are also useful.

The amount of detergent amine used in the fuel is typically between 0.01 and about 100 pounds per thousand barrels of fuel (0.0000004 to 0.004 weight percent), preferably between 1 and about 50 pounds per thousand barrels and most preferably between 1 and about 30 pounds per thousand barrels. Smaller amounts of amine than those indicated do not appear to have much if any detergent effect as indicated by the buildup of intake valve deposits. On the other hand, larger amounts are not required to prevent the formation and buildup of intake valve deposits.

The second constituent in the intake valve deposit control additive of this invention is a fuel dispersant selected from the group consisting of polyalkylamines and Mannich bases. Polyalkyl amines are defined herein as being limited to amines other than monoalkyl primary mono-amines containing at least one substantially olefin-free, aliphatic, hydrocarbyl radical free of alkynyl unsaturation, said radical having been formed at least in part by the polymerization or copolymerization of one or more olefins. Preferably in the present invention, the polyalkylamine dispersants are high

molecular weight branched chain aliphatic hydrocarbon N-substituted amines or alkylene polyamines, said amines and polyamines having molecular weights from about 150 to about 5,000. Particularly preferred compositions in the present invention will have the following formula:



wherein s indicates that the ring structure shown is fully saturated, A is hydrogen, a hydrocarbyl group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbyl group having from 1 to about 10 carbon atoms, X is hydrogen, a hydrocarbon group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbyl group having from 1 to about 10 carbon atoms, with either of said groups being optionally taken with A to form a ring of from 5 to 6 annular atoms and up to about 12 carbon atoms, U is an alkylene group of from 2 to about 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms shown, R is an aliphatic radical of from about 40 to about 5000 average molecular weight, a is an integer from 1 to about 10, b is an integer from 0 to 1 with the sum of $a + 2b$ being an integer from 1 to 10, c is an integer of from 1 to 5 and equal to or less than the number of nitrogen atoms in the molecule, x and y are both 0 or 1, with the sum of x and y being equal to 1.

The hydrocarbon radical indicated by R is relatively free of aliphatic unsaturation; that is, it will usually have not more than two sites of olefinic unsat-

uration, preferably not more than one site of olefinic unsaturation, and no acetylenic unsaturation.

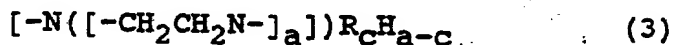
Polyalkyl monoamine compositions for this use have the general formula:



wherein R is a branched chain aliphatic radical, substantially free of olefinic unsaturation, and A is a lower alkyl group. R is preferably an alkyl group.

Illustrative of suitable polyalkyl monoamine dispersants conforming to this formula are polypropyl amine, polyisobutyl amine, N-polyisobutyl dimethyl amine, N-polyisobutyl methylethylamine, N-polypropyl diethyl amine, N-polypropyl di(2-hydroxyethyl) amine, N-polyisobutyl N-methyl aniline, N-polyisobutyl morpholine, N-polyisobutyl piperidine, N-poly(sec-butene) propylamine, N-polypropyl N-(2-hydroxyethyl) amine, etc. Preferred for this use are those amines wherein R has a molecular weight from about 40 to about 1250 and A has between 1 and about 3 carbon atoms.

Polyalkyl polyamine dispersant compositions preferred in this invention conform generally to formula (3) as shown below:



wherein a is an integer between 1 and about 5, c is an integer between 1 and about 3, and R is a branched chain aliphatic radical. The dispersant may be comprised of monosubstituted polyamines wherein R is a

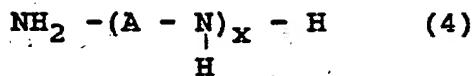
branched hydrocarbon chain derived from polymerizing olefins of from 2 to about 6 carbon atoms. Illustrative compounds useful for this purpose include N-polyisobutyl ethylene diamine, N-polypropyldiamine, N-poly(1-butenyl) ethylene diamine, N-(alternating copolymer of ethylene and isobutylene) ethylene diamine, N-polypropyl 2-aminoethylpiperazine, N-polyisobutyl 2-aminoethylpiperazine, N-polypropyl diethylene triamine, N-polyisobutyl diethylene triamine, N-poly(1-pentenyl) or diethylene triamine, N-polypropyl trimethylene diamine, N-polyisobutyl trimethylene diamine, N-polypropyl di-(trimethylene) triamine, N-polyisobutyl di-(trimethylene) triamine, N-polyisobutyl 1,2-propylene diamine, N-polyisobutenyl di-(1,2-propylene) triamine, N-polypropyl triethylene tetramine, N-polyisobutyl triethylene tetramine, N-(alternating copolymer of ethylene and isobutylene) triethylene tetramine, N-polypropyl tetraethylene pentamine, N-polyisobutyl tetraethylene pentamine, N-polyisobutyl pentaethylene hexamine, etc.

Suitable dispersants may also be prepared from polyhydrocarbon radical substituted alkylene polyamine compositions. Illustrative compounds are N,N'-di(polypropyl) diethylene triamine, N,N'-di(polyisobutyl) diethylene triamine, N,N'-di(isobutyl) triethylene tetramine, N,N'-di(polypropyl) tetraethylene pentamine, N,N'-di(polyisobutyl) tetraethylene pentamine, N,N'N"-tri(polyisobutyl) tetraethylene pentamine, N,N'-di(polyisobutyl) 2-aminoethylpiperazine, N,N'-di(poly 1-butyl) triethylene tetramine, N,N'-di(polyisobutyl) di(trimethylene) triamine, etc.

Most preferred for the purposes of the present invention are the straight chain alkylene polyamines, particularly ethylene diamine and polyethylene polyamines, wherein n of formula (3) is from 1 to about 4, and R is a branched chain aliphatic radical having an average molecular weight ranging from about 40 to about 1500, preferably alkyl groups, most preferably polypropyl or polyisobutyl, and with the polyamine having fewer R groups than nitrogen atoms.

Synthesis procedures for preparing polyalkylamines conforming to the above definitions are given by Honnen et al. in U.S. Patent 3,438,757, which is incorporated herein by reference, in its entirety.

In a second embodiment of the present invention, the dispersant constituent comprises one or more compounds known as Mannich bases. These are condensation products formed by reacting an alkyl substituted hydroxy substituted aromatic compound, an aldehyde and an amine. Typically, for Mannich base dispersants preferred in the present invention, the alkyl substituent has an average molecular weight in the range between about 100 to about 100,000, and the compound is preferably a polyalkyl phenol whose alkyl component is derived from 1-mono-olefinic polymers having an average molecular weight ranging between about 100 and about 3000, the aldehyde is a low molecular weight aldehyde, and the amine has at least one $>NH$ group and is preferably an alkylene polyamine of the formula:



wherein A is a divalent alkylene radical having from about 2 to about 6 carbon atoms and x is an integer ranging from 1 to about 10.

The foregoing condensation product is prepared according to conventional methods heretofore employed and well known in the art for preparing Mannich type products. For the purposes of the present invention, it is preferred the the molar ratios of the alkyl substituted hydroxyaromatic compound, amine and aldehyde be between about 1:1:10 to about 10:0.1:10.

Representative of the alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol and other polyalkylphenols. The alkyl substituents thereon may be derived from polypropylenes, polybutenes and other polymers of mono-olefins, principally 1-mono-olefins. Also useful are copolymers of mono-olefins with monomers copolymerizable therewith, wherein the copolymer molecule comprises at least 90%, by weight, of mono-olefinic units. Specific examples are copolymers of butenes (butene-1, butene-2 and isobutylene) with monomers copolymerizable therewith wherein the copolymer molecule contains at least 90%, by weight, of propylene and butene units, respectively. The copolymerizable monomers may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, methyl styrene, p-dimethyl styrene, divinyl benzene, and the like.

In addition to these alkyl substituted hydroxyaromatic compounds, others which may be used include, exclusive of sulfurized derivatives, alkyl-substituted derivatives of resorcinol, hydroquinone, cresol, catechol, xylenol, hydroxy diphenyl, benzylphenol, phenethylphenol, naphthol, tolynaphthol, among others. Preferred, however, are polyalkylphenol reactants, e.g., polypropylphenol and polybutylphenol whose alkyl group has an average molecular weight between about 100 and 3000 with the preferred configuration being that of a para-substituted mono-alkylphenol.

Representative amine reactants are alkylene polyamines, particularly polyethylene amines. Other representative organic compounds containing at least one >NH group suitable for use herein include the mono- and diamino alkanes and their substituted analogs, e.g., ethylamine, dimethylamine, dimethyl aminopropyl amine and dimethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthylenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidiazol, imidiazolidine and piperidine; melamine and their substituted analogs.

Suitable alkylene polyamine reactants include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene heptamine, heptaethylene octamine, octaethylene nonamine, nonaethylene decamine, decaethylene undecamine and mixtures of such amines having nitrogen contents corresponding to the alkylene polyamines in formula (4) above, with A therein being

divalent ethylene. Corresponding polypropylene polyamines such as propylene diamine and di-, tri-, tetra-, penta-propylene tri-, tetra-, penta- and hex-amines are also suitable as reactants.

Representative aldehydes for use herein include the aliphatic aldehydes such as formaldehyde (including paraformaldehyde and Formalin), acetaldehyde, and aldol, (b-hydroxybutyraldehyde) with formaldehyde or a formaldehyde-yielding reactant.

Techniques for forming Mannich dispersants according to the above description are given by Udelhofen et al. in U.S. Patent 4,231,759, the contents of which are incorporated herein in their entirety, by reference.

Concentrations of either the polyalkylamine or Mannich base dispersant in the fuel are typically between 0.1 and about 200, preferably between about 10 and about 100, more preferably between about 10 and about 85, and most preferably between about 10 and about 75 pounds per thousand barrels of gasoline fuel.

The third constituent in the intake valve deposit control additive of the present invention is a fluidizer oil. These oils are believed act as a carrier for the other detergent/dispersant additives and to assist in removing and preventing deposits. One suitable oil for this purpose is a nonvolatile lubricating mineral oil, particularly a refined naphthenic lubricating oil having a viscosity, at 100° F, of between about 500 and 2,000 SUS. Another is a polyolefin carrier, particu-

larly polypropylene or polybutene having a molecular weight in the range from about 600 to about 3000. In the present invention, such oils are typically added to provide a concentration in the range from about 20 to 300 pounds, preferably between about 50 to about 200 pounds per thousand barrels of gasoline fuel.

The concentration of intake valve deposit control additive formulated as hereinabove is preferably between about 50 and 600 pounds per thousand barrels of fuel, with between about 75 and about 500 being more preferred and between about 100 to about 300 being most preferred.

The intake valve deposit control additive of the present invention can be added, with success, to either leaded gasolines or unleaded gasolines such as those used with catalytic convertors. An unleaded gasoline is defined as one containing less than 0.05 grams of lead per gallon of gasoline.

Liquid hydrocarbons fuels suitable for combustion in automotive multport-injected internal combustion engines are usually mixtures of hydrocarbons boiling in the range from about 100° F. to about 437° F., and often comprise mixtures of saturated hydrocarbons, olefinic hydrocarbons and aromatic hydrocarbons. Preferred are gasoline blends comprising a mixture having a saturated hydrocarbon content ranging from about 40 to about 80 percent, by volume, an olefinic content from about 0 to about 30 percent, by volume, and an aromatic content ranging from about 10 to about

60 percent, by volume. The base fuel can be derived from straight run gasoline, polymer gasoline, natural gasoline, dimer and trimer olefins, synthetically-produced hydrocarbon mixtures derived from coal or shale oil, from thermally or catalytically reformed hydrocarbons, from thermally or catalytically cracked petroleum stocks, and mixtures of these. While the hydrocarbon composition and octane level of the gasoline base fuel are not critical, the composition and octane level typically considered to constitute a commercial grade of unleaded fuel are preferred.

Normally, the hydrocarbon mixtures to which the intake deposit reducing additive composition of the present invention is applied are substantially lead-free but may contain minor amounts of blending agents such as methanol, ethanol, methyl tertbutyl ether (MTBE), and the like. The fuel may also contain antioxidants such as phenolics, e.g., 2,6 di-tert-butylphenol or phenolenediamines, metal deactivators, deha-zors such as polyester-type ethoxylated alkylphenol formaldehyde resins and the like. The fuel may also contain anti-knock compounds such as tetraethyl lead, a methyl cyclopentadienyl manganese tricarbonyl, orthoazidophenol and the like. Dyes, dispersants, corrosion inhibitors, anti-icing agents, demulsifiers and deposit modifiers can also be contained in the fuels. Preferably, however, such additives do not contain lead.

The intake valve deposit control additive of the present invention can be introduced into an operating engine in a variety of ways. The additive can be

injected directly into the intake manifold intermittently or substantially continuously, preferably in a hydrocarbon carrier suitable for combustion in a spark-ignited internal combustion engine, usually having a final boiling point (by ASTM D86) lower than about 437° F. A preferred method is to incorporate the additive into the gasoline blend. In so doing the additive can be added separately to the gasoline or blended with other gasoline additives.

The invention further provides a concentrate, dissolvable or miscible in gasoline, comprising: (a) from about 50 to about 4000 grams per gallon of the hereinabove described intake valve deposit control additive, and (b) optionally from about 0.01 to about 0.2 weight percent of a dehazer with the balance being a diluent suitable for combustion in a multiport fuel injected internal combustion engine, said diluent usually boiling in the range from about 100° F to about 437° F. The ratio of the concentrations of the individual constituents in the total additive blend will be about the same as given hereinabove for those in the fuel, i.e., the amine will be comprised of between 0.1 to about 100, preferably 1 to about 50 and most preferably 1 to about 30 parts, by weight, the dispersant 1 to about 200, preferably about 10 to about 100 and most preferably about 10 to about 95 and very most preferably about 10 to about 75 parts, by weight, and the fluidizer 20 to about 300, and preferably 50 to about 200 parts, by weight, for each liquid unit of additive. Diluents may include hydrocarbons and oxygen-containing hydrocarbons. Suitable oxygen-containing hydrocarbons

include methanol, ethanol, propanol, methyl-tert-butyl ether, and ethylene glycol monobutyl ether. The hydrocarbon diluent may be an alkane such as heptane but is preferably an aromatic hydrocarbon such as toluene or xylene, alone or in admixture with said oxygen-containing hydrocarbon diluents. The optional dehazer is usually a polyester-type ethoxylated alkyl phenolformaldehyde resin, but is not specifically limited thereto. A sufficient amount of concentrate should be used to assure that concentration in the fuel is as defined hereinabove.

When the additive of the present invention is used in a gasoline fuel, it is found that a relatively low concentration of dispersant in the fuel will reverse any intake valve deposit forming tendencies exhibited by the amine detergent constituent and, therefore, produce a total composition suitable for BMW certification. Likewise, the use of the additive of the invention enables the use of far less dispersant to be effective for intake valve deposit control. In other words, the combination of detergent and dispersant components in the present invention achieves two important results simultaneously: (1) the dispersant overcomes the deposit-promoting effect of the C_6+ primary amine detergent, and (2) the amine allows for a substantial reduction in the amount of dispersant needed to remove deposits than would otherwise be the case if the dispersant were used alone. This reduction in dispersant level means that fuels containing the additive of the present invention will substantially improve engine performance with a lower intake valve

deposit controlling additive cost than heretofore possible. This is because the dispersant is relatively far more expensive than the detergent.

The following example demonstrates the the surprising reduction in intake valve deposits and performance improvement achieved when using a fuel containing the intake valve deposit control additive of the present invention. This example is meant to be illustrative of the present invention and are not intended to limit the scope of the appended claims.

EXAMPLE 1

A series of tests were conducted per the procedure for the "BMW 100 Hour Valve Deposit Cycle Program," as described by Bitting et al. in their aforementioned paper. For these runs a total of five different gasoline formulations were prepared. Prior to the start of each test, the intake valves of a BMW 318i 4 cylinder engine (used in tests 1 through 3) or a BMW 325i 6 cylinder engine (used in tests 4 and 5) were removed, rinsed with hexane until the wash was clear, dried in an oven at 200° F for 5 minutes and, after cooling in a desiccator for an hour, weighed to the nearest 0.1 mg. For each test run new valve seals, fresh oil, and a new oil filter were used, and the ignition and valve lash set according to factory specifications. The gasoline used in all of the test runs was a base fuel used commercially in premium unleaded fuels with the general composition shown in table 1.

TABLE 1

GASOLINE FUEL CHARACTERISTICS

Characteristic	
Gravity @ 60° F. (°API)	55.9
Research octane no.	94.4
Motor octane no.	84.6
Reid vapor pressure (PSI)	8.7
FIA (D319) wt %	
Aromatics	33.0
Olefins	6.5
Saturates	60.5
Distillation (D 86) ° F	
initial	96
10%	125
30%	184
50%	225
70%	266
90%	334
95%	360
End point	420
Sulfur (ppm)	250
% Carbon	86.5

Each of the tests was stopped after 5000 miles and again after 10,000 miles of operation at which time the intake valves were visually inspected and reweighed. The results obtained are shown in table 2. Note that the oleyl amine when used by itself as an intake valve detergent (test 2) provided a level of valve deposit formation and buildup which was higher than that found when the base fuel was used "neat" (test 1). Also note that when the compositions of the present invention were used (tests 3 and 4), the levels of intake valve deposition were all well below the BMW test criterion.

Therefore it can be seen that, when an intake valve deposit control additive, as described herein

above, is incorporated into fuel used in a new or clean engine, intake valve deposit formation and buildup increase at a sufficiently low rate that the fuel will easily meet the criterion established in the BMW test procedure previously referenced.

While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those of skill in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations as fall within the scope and spirit of the appended claims.

We claim:

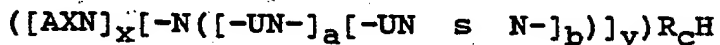
1. A fuel composition comprising a gasoline suitable for combustion in an automotive spark-ignited internal combustion engine, said gasoline having dissolved therein an additive combination comprising one or more C_6+ primary amines, one or more gasoline dispersants selected from the group consisting of polyalkylamines and Mannich bases, and a nonvolatile fluidizer oil.

2. The fuel composition of claim 1 wherein said primary amines have the formula RNH_2 , wherein R is either (1) an alkyl or akenyl radical having from about 12 to about 22 carbon atoms or (2) a radical of the form $R-O-R'$ wherein R and R' are independently selected from the group consisting of C_2 to C_{20} aliphatic radicals, hydrocarbyl radicals, alkyl radicals and alkenyl radicals and the total number of carbon atoms in R and R' combined is between about 10 and about 30, with said amines being present in said fuel in a concentration between about 0.1 and about 100 PTB.

3. The fuel composition of claim 1 wherein said primary amine is an alkyl or akenyl radical having from about 12 to about 18 carbon atoms and is present in a concentration between 1 and about 50 PTB.

4. The fuel composition of claim 3 wherein said amine is oleyl amine and is present in a concentration between 1 and about 30 PTB.

5. The fuel composition of claim 1 wherein said fuel dispersant is a polyalkylamine having the following formula:



wherein s indicates the ring structure shown to be fully saturated, A is hydrogen, a hydrocarbon group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbon group having from 1 to about 10 carbon atoms, X is hydrogen, a hydrocarbon group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbon group having from 1 to about 10 carbon atoms, with either of said groups being optionally taken with A to form a ring of from 5 to 6 annular members and up to about 12 carbon atoms total, U is an alkylene group of from 2 to about 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms, R is an aliphatic radical of from about 400 to about 5000 average molecular weight, a is an integer from 0 to 10, b is an integer from 0 to 1 with the sum of $a + 2b$ being an integer from 1 to 10, c is an integer of from 1 to 5 and equal to or less than the number of nitrogen atoms in the molecule, x and y are both 0 or 1, with the sum of x and y being equal to 1.

6. The fuel composition of claim 5 wherein $y = 0$ and said dispersant is a polyalkyl monoamine selected from the group consisting of polypropyl amine, polyisobutyl amine, N-polyisobutyl dimethyl amine, N-polyisobutyl methylethylamine, N-polypropyl diethyl amine, N-polypropyl di(2-hydroxyethyl) amine, N-polyi-

sobutyl N-methyl aniline, N-polyisobutyl morpholine, N-polyisobutyl piperidine, N-poly(1-butene) propylamine and N-polypropyl N-(2-hydroxyethyl) amine and is present in a concentration between 1 and about 200 PTB.

7. The fuel composition of claim 6 wherein said monoamine has the general formula:



wherein R is a branched chain aliphatic radical, substantially free of olefinic unsaturation, of from about 40 to about 1250 average molecular weight and A is a lower alkyl having from 1 to about 3 carbon atoms and is present in a concentration between about 10 and 100 PTB.

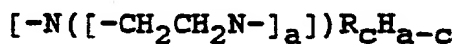
8. The fuel composition of claim 5 wherein $y = 1$, $x = 0$, U is $(CH_2)_d$, with d being 2 or 3, R is a branched hydrocarbon chain having from 2 to about 6 carbon atoms and having an average molecular weight in the range of 40 to 3000 and said dispersant is a polyalkyl polyamine.

9. The fuel composition of claim 8 wherein said polyamine is selected from the group consisting of N-polyisobutyl ethylene diamine, N-polypropyldiamine, N-poly(1-butyl) ethylene diamine, N-(alternating copolymer of ethylene and isobutylene) ethylene diamine, N-polypropyl 2-aminoethylpiperazine, N-polyisobutyl 2-aminoethylpiperazine, N-polypropyl diethylene triamine, N-polyisobutyl diethylene triamine, N-poly(1-pentyl) diethylene triamine, N-polypropyl trimethylene diamine, N-polyisobutyl trimethylene diamine, N-polypropyl di-

(trimethylene) triamine, N-polyisobutyl di-(trimethylene) triamine, N-polyisobutyl 1,2-propylene diamine, N-polyisobutyl di-(1,2-propylene) triamine, N-polypropyl triethylene tetramine, N-polyisobutyl triethylene tetramine, N-(alternating copolymer of ethylene and isobutylene) triethylene tetramine, N-polypropyl tetraethylene pentamine, N-polyisobutyl tetraethylene pentamine and N-polyisobutyl pentaethylene hexamine, and is present in a concentration between 1 and about 200 PTB.

10. The fuel composition of claim 8 wherein said polyamine is a polyhydrocarbon radical substituted alkylene polyamine composition selected from the group consisting of N,N'-di(polypropyl) diethylene triamine, N,N'-di(polyisobutyl) diethylene triamine, N,N'-di(isobutyl) triethylene tetramine, N,N'-di(polypropyl) tetraethylene pentamine, N,N'-di(polyisobutyl) tetraethylene pentamine, N,N'N"-tri(polyisobutyl) tetraethylene pentamine, N,N'-di(polyisobutyl) 2-aminoethylpiperazine, N,N'-di(poly 1-butyl) triethylene tetramine and N,N'-di(polyisobutyl) di(trimethylene) triamine, and is present in a concentration between 1 and about 200 PTB.

11. The fuel composition of claim 8 wherein said polyamine is a straight chain polyamine having the following formula:



wherein a is an integer from 1 to 5, c is an integer from 1 to 3, R is a polypropyl or polyisobutyl radical

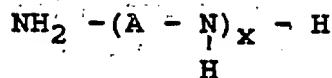
having an average molecular weight ranging from about 40 to about 3000, said amine having fewer R groups than nitrogen atoms and being present in a concentration between 10 and about 100 PTB.

12. The fuel composition of claim 5 wherein said dispersant is present in a concentration between about 10 and about 75 PTB.

13. The fuel composition of claim 1 wherein said dispersant is a Mannich base, said base being the condensation product of an alkyl substituted hydroxy substituted aromatic compound, an aldehyde and an amine with the alkyl substituent having an average molecular weight in the range between about 100 to about 100,000, said base being present in a concentration between 1 and about 200 PTB.

14. The fuel composition of claim 13 wherein said alkyl substituent has an average molecular weight in the range between about 100 to about 5,000, the aldehyde is a low molecular weight aldehyde and the amine has at least one >NH group, said base being present in a concentration between about 10 and 100 PTB.

15. The fuel composition of claim 14 wherein said hydroxy substituted aromatic compound is a polyalkyl phenol whose alkyl component is derived from 1-mono-olefinic polymers having an average molecular weight ranging between about 100 and about 3000, the aldehyde is formaldehyde and the amine is an alkylene polyamine of the formula:



wherein A is a divalent alkylene radical having from about 2 to about 6 carbon atoms and x is an integer ranging from 1 to about 10.

16. The fuel composition of claim 15 wherein said polyalkyl phenol is selected from the group consisting of para substituted, mono-alkyl polypropylphenol and polybutylphenol, said amine is an alkylene polyamine and the mola ratio of alkyl substituted phenol, aldehyde and amine is between about 1:1:10 and about 10:0.1:10 and the concentration of dispersant present ranges between about 10 and about 75 PTB.

17. The fuel composition of claim 1 wherein said nonvolatile fluidizer is selected from the group consisting of a lubricating mineral oil having a viscosity, at 100° F, of between about 500 and 2000 SUS, and a polyolefin oil having an average molecular weight between about 600 and about 3000, and has a concentration between about 50 and about 300 PTB.

18. The fuel composition of claim 18 wherein said mineral oil is a refined naphthenic oil, said polyolefin oil is polypropylene or polybutene and said fluidizer is present in a concentration between 50 and about 200 PTB.

19. The fuel composition of claim 1 wherein said gasoline fuel is a blend comprising a mixture having a

saturated hydrocarbon content ranging from about 40 to about 80 percent, by volume, an olefinic content from about 0 to about 30 percent, by volume, and an aromatic content ranging from about 10 to about 60 percent, by volume and additive concentration is between about 50 and 600 PTB of a mixture comprising between 0.1 and about 100 parts, by weight, of a C₆+ primary aliphatic amine, between 1 and about 200 parts, by weight, of a fuel dispersant and between about 20 and about 300 parts, by weight, of a fluidizer.

20. The fuel composition of claim 19 wherein intake valve deposit controlling additive concentration is between about 75 and about 500 pounds PTB.

21. The fuel composition of claim 19 wherein the fuel is an unleaded gasoline and said additive concentration is between about 100 and about 300 PTB.

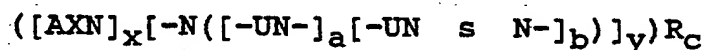
22. A method for controlling the depositon of intake valve deposits in lean-burn, high compression, spark-ignited internal combustion engines comprising introducing into said engine a fuel composition comprising a gasoline suitable for combustion in an automotive spark-ignited internal combustion engine, said gasoline having dissolved therein an intake valve deposit controlling amount of an intake valve deposit additive, said additive comprising one or more C₆+ primary amines, one or more gasoline dispersants selected from the group consisting of one or more polyalkylamines and Mannich bases, and a nonvolatile fluidizer oil.

23. The method of claim 22 wherein wherein said primary amines have the formula RNH_2 , wherein R is either (1) an alkyl or akenyl radical having from about 12 to about 22 carbon atoms or (2) a radical of the form $R-O-R'$ wherein R and R' are independently C_2 to C_{20} aliphatic radicals, hydrocarbyl radicals, alkyl radicals and alkenyl radicals, and the total number of carbon atoms in R and R' combined is between about 10 and about 30, with said amines being present in said additive mixture in a concentration amount between about 0.1 and about 100 PTB.

24. The method of claim 23 wherein said primary primary amine is an alkyl or akenyl radical having from about 12 to about 18 carbon atoms and is present in a concentration between 1 and about 50 PTB.

25. The method of claim 24 wherein said amine is oleyl amine and is present in a concentration between 1 and about 30 PTB.

26. The method of claim 22 wherein said fuel dispersant is a polyalkylamine having the following formula:



wherein s indicates the ring structure shown to be fully saturated, A is hydrogen, a hydrocarbon group

having from 1 to about 10 carbon atoms or a hydroxyhydrocarbon group having from 1 to about 10 carbon atoms, X is hydrogen, a hydrocarbon group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbon group having from 1 to about 10 carbon atoms, with either of said groups being optionally taken with A to form a ring of from 5 to 6 annular members and up to about 12 carbon atoms total, U is an alkylene group of from 2 to about 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms, R is an aliphatic radical of from about 400 to about 5000 average molecular weight, a is an integer from 0 to 10, b is an integer from 0 to 1 with the sum of $a + 2b$ being an integer from 1 to 10, c is an integer of from 1 to 5 and equal to or less than the number of nitrogen atoms in the molecule, x and y are both 0 or 1, with the sum of x and y being equal to 1.

27. The method of claim 26 wherein $y = 0$ and said dispersant is a polyalkyl monoamine selected from the group consisting of polypropyl amine, polyisobutyl amine, N-polyisobutyl dimethyl amine, N-polyisobutyl methylethylamine, N-polypropyl diethyl amine, N-polypropyl di(2-hydroxyethyl) amine, N-polyisobutyl N-methyl aniline, N-polyisobutyl morpholine, N-polyisobutyl piperidine, N-poly(1-butene) propylamine and N-polypropyl N-(2-hydroxyethyl) amine and is present in a concentration between 1 and about 200 PTB.

28. The method of claim 24 wherein said dispersant comprises a monoamine of the general formula:



wherein R is a branched chain aliphatic radical, substantially free of olefinic unsaturation, of from about 40 to about 1250 average molecular weight and A is a lower alkyl having from 1 to about 3 carbon atoms, and is present in a concentration between about 10 and 100 PTB.

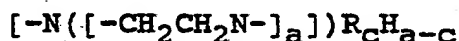
29. The method of claim 27 wherein $y = 1$, $x = 0$, U is $(CH_2)_d$, with d being 2 or 3, R is a branched hydrocarbon chain having from 2 to about 6 carbon atoms and having an average molecular weight in the range of 400 to 3000 and said dispersant is a polyalkyl polyamine.

30. The method of claim 25 wherein said dispersant comprises a polyalkyl polyamine selected from the group consisting of N-polyisobutyl ethylene diamine, N-polypropyldiamine, N-poly(1-butyl) ethylene diamine, N-(alternating copolymer of ethylene and isobutylene) ethylene diamine, N-polypropyl 2-aminoethylpiperazine, N-polyisobutyl 2-aminoethylpiperazine, N-polypropyl diethylene triamine, N-polyisobutyl diethylene triamine, N-poly(1-pentyl) diethylene triamine, N-polypropyl trimethylene diamine, N-polyisobutyl trimethylene diamine, N-polypropyl di-(trimethylene) triamine, N-polyisobutenyl di-(trimethylene) triamine, N-polyisobutyl 1,2-propylene diamine, N-polyisobutyl di-(1,2-propylene) triamine, N-polypropyl triethylene tetramine, N-polyisobutyl triethylene tetramine, N-(alternating copolymer of ethylene and isobutylene) triethylene tetramine, N-polypropyl tetraethylene pentamine, N-polyisobutyl tetraethylene pentamine and N-polyisobutyl

penta thylene hexamine, and is present in a concentration between 1 and about 200 PTB.

31. The method of claim 24 wherein said dispersant comprises a polyamine is a polyhydrocarbon radical substituted alkylene polyamine composition selected from the group consisting of N,N'-di(polypropyl) diethylene triamine, N,N'-di(polyisobutyl) diethylene triamine, N,N'-di(isobutyl) triethylene tetramine, N,N'-di(polypropyl) tetraethylene pentamine, N,N'-di(polyisobutyl) tetraethylene pentamine, N,N'N"-tri(polyisobutyl) tetraethylene pentamine, N,N'-di(polyisobutyl) 2-aminoethylpiperazine, N,N'-di(poly 1-butyl) triethylene tetramine and N,N'-di(polyisobutyl) di(trimethylene) triamine, and is present in a concentration between 1 and about 200 PTB.

32. The method of claim 24 wherein said dispersant comprises a straight chain polyamine having the following formula:



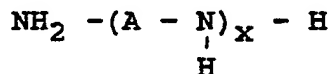
wherein a is an integer from 1 to 5, c is an integer from 1 to 3, R is a polypropyl or polyisobutyl radical having an average molecular weight ranging from about 40 to about 3000, said amine having fewer R groups than nitrogen atoms and being present in a concentration between 10 and about 100 PTB.

33. The method of claim 26 wherein said dispersant is present in a concentration between about 10 and about 75 PTB.

34. The method of claim 24 wherein said dispersant is a Mannich base, said base being the condensation product of an alkyl substituted hydroxy substituted aromatic compound, an aldehyde and an amine with the alkyl substituent having an average molecular weight in the range between about 100 to about 100,000, said base being present in a concentration between 1 and about 200 PTB.

35. The method of claim 34 wherein said alkyl substituent has an average molecular weight in the range between about 100 to about 5,000, the aldehyde is a low molecular weight aldehyde and the amine has at least one >NH group, said base being present in a concentration between about 10 and 100 PTB.

36. The method of claim 35 wherein said hydroxy substituted aromatic compound is a polyalkyl phenol whose alkyl component is derived from 1-mono-olefinic polymers having an average molecular weight ranging between about 100 and about 3000, the aldehyde is formaldehyde and the amine is an alkylene polyamine of the formula:



wherein A is a divalent alkylene radical having from about 2 to about 6 carbon atoms and x is an integer

ranging from 1 to about 10.

37. The method of claim 36 wherein said polyalkyl phenol is selected from the group consisting of para substituted, mono-alkyl polypropylphenol and polybutylphenol, said amine is an alkylene polyamine and the mola ratio of alkyl substituted phenol, aldehyde and amine is between about 1:1:10 and about 10:0.1:10 and the amount of dispersant present ranges between 10 and 50 PTB.

38. The method of claim 34 wherein said nonvolatile fluidizer is selected from the group consisting of a lubricating mineral oil having a viscosity, at 100° F, of between about 500 and 2000 SUS, and a polyolefin oil having an average molecular weight between about 600 and 300, in a concentration between about 20 and about 300 PTB.

39. The method of claim 33 wherein fluidizer is a refined naphthenic oil, or a polypropylene or polybutylene oil and is present in a concentration between 50 and about 200 PTB.

40. The method of claim 22 wherein said gasoline fuel is a blend comprising a mixture having a saturated hydrocarbon content ranging from about 40 to about 80 percent, by volume, an olefinic content from about 0 to about 30 percent, by volume, and an aromatic content ranging from about 10 to about 60 percent, by volume and said additive concentration is no more than about about 600 PTB of a mixture comprising between 0.1 and

about 100 parts, by weight, of a C_6+ primary aliphatic amine, between 1 and about 200 parts, by weight, of a fuel dispersant and between about 20 and about 300 parts, by weight, of a fluidizer.

41. The method of claim 40 wherein the concentration of said intake valve deposit controlling additive in said fuel is between about 75 and about 500 PTB.

42. The method of claim 22 wherein said fuel is an unleaded gasoline and said additive concentration is between about 100 and about 300 PTB.

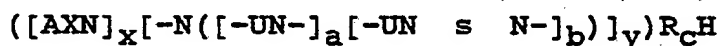
43. An intake valve deposit controlling additive composition for use with fuel compositions used in spark-ignited internal combustion engines said additive comprising one or more primary amine carburetor detergents, one or more gasoline dispersants selected from the group consisting of one or more polyalkylamines and Mannich bases, and a nonvolatile fluidizer oil.

44. The additive composition of claim 43 wherein said primary amines have the formula RNH_2 , wherein R is either (1) an alkyl or alkenyl radical having from about 12 to about 22 carbon atoms or (2) a radical of the form $R-O-R'$ wherein R and R' are independently C_2 to C_{20} aliphatic radicals, hydrocarbyl radicals, alkyl radicals and alkenyl radicals, and the total number of carbon atoms in R and R' combined is between about 10 and about 30, said amine being present in a concentration between about 0.1 and 100 parts, by weight, in said additive composition.

45. The additive composition of claim 43 wherein said primary primary amine is an alkyl or akenyl radical having from about 12 to about 18 carbon atoms and is present in a concentration between about 1 and about 50 parts, by weight.

46. The additive composition of claim 45 wherein said amine is oleyl amine and is present in a concentration between about 1 and about 30 parts, by weight.

47. The additive composition of claim 43 wherein said fuel dispersant is a polyalkylamine having the following formula:



wherein s indicates the ring structure shown to be fully saturated, A is hydrogen, a hydrocarbon group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbon group having from 1 to about 10 carbon atoms, X is hydrogen, a hydrocarbon group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbon group having from 1 to about 10 carbon atoms, with either of said groups being optionally taken with A to form a ring of from 5 to 6 annular members and up to about 12 carbon atoms total, U is an alkylene group of from 2 to about 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms, R is an aliphatic radical of from about 400 to about 5000 average molecular weight, a is an integer from 0 to 10, b is an integer from 0 to 1 with the sum of a + 2b being an

integer from 1 to 10, c is an integer of from 1 to 5 and equal to or less than the number of nitrogen atoms in the molecule, x and y are both 0 or 1, with the sum of x and y being equal to 1, said dispersant being present in a concentration between 1 and about 200 parts, by weight, in said composition.

48. The additive composition of claim 47 wherein $y = 0$ and said dispersant is a polyalkyl monoamine selected from the group consisting of polypropyl amine, polyisobutyl amine, N-polyisobutyl dimethyl amine, N-polyisobutyl methylethylamine, N-polypropyl diethyl amine, N-polypropyl di(2-hydroxyethyl) amine, N-polyisobutyl N-methyl aniline, N-polyisobutyl morpholine, N-polyisobutyl piperidine, N-poly(1-butene) propylamine and N-polypropyl N-(2-hydroxyethyl) amine.

49. The additive composition of claim 48 wherein said monoamine has the general formula:



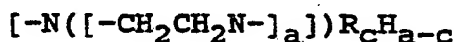
wherein R is a branched chain aliphatic radical, substantially free of olefinic unsaturation, of from about 40 to about 1250 average molecular weight and A is a lower alkyl having from 1 to about 3 carbon atoms, and said amine is present in a concentration between 1 and about 75 parts, by weight.

50. The additive composition of claim 47 wherein $y = 1$, $x = 0$, U is $(CH_2)_d$, with d being 2 or 3, R is a branched hydrocarbon chain having from 2 to about 6 carbon atoms and having an average molecular weight in the range of 400 to 3000 and said dispersant is a

polyalkyl polyamine.

51. The additive composition of claim 50 wherein said polyamine is a polyhydrocarbon radical substituted alkylene polyamine composition selected from the group consisting of N,N'-di(polypropyl) diethylene triamine, N,N'-di(polyisobutyl) diethylene triamine, N,N'-di(isobutyl) triethylene tetramine, N,N'-di(polypropyl) tetraethylene pentamine, N,N'-di(polyisobutyl) tetraethylene pentamine, N,N'-tri(polyisobutyl) tetraethylene pentamine, N,N'-di(polyisobutyl) 2-aminoethylpiperazine, N,N'-di(poly 1-butene) triethylene tetramine and N,N'-di(polyisobutyl) di(trimethylene) triamine, and is present in a concentration between 1 and about 200 parts by weight.

52. The additive composition of claim 50 wherein said polyamine is a straight chain polyamine having the following formula:



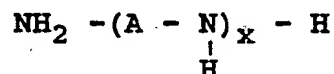
wherein a is an integer from 1 to 5, c is an integer from 1 to 3, R is a polypropyl or polyisobutyl radical having an average molecular weight ranging from about 40 to about 3000, said amine having fewer R groups than nitrogen atoms and being present in a concentration between 10 and about 100 parts by weight.

53. The additive composition of claim 43 wherein said dispersant is present in a concentration between about 10 and about 75 parts by weight.

54. The additive composition of claim 43 wherein said dispersant is a Mannich base, said base being the condensation product of an alkyl substituted hydroxy substituted aromatic compound, an aldehyde and an amine with the alkyl substituent having an average molecular weight in the range between about 100 to about 100,000.

55. The additive composition of claim 54 wherein the molecular weight of said alkyl group is between about 100 and about 5000, the aldehyde is a low molecular weight aldehyde and the amine has at least one >NH group.

56. The additive composition of claim 55 wherein said hydroxy substituted aromatic compound is a polyalkyl phenol whose alkyl component is derived from 1-mono-olefinic polymers having an average molecular weight ranging between about 100 and about 3000, the aldehyde is formaldehyde and the amine is an alkylene polyamine of the formula:



wherein A is a divalent alkylene radical having from about 2 to about 6 carbon atoms and x is an integer ranging from 1 to about 10.

57. The additive composition of claim 56 wherein said polyalkyl phenol is selected from the group consisting of para substituted, mono-alkyl polypropylphenol and polybutylphenol, said amine is an alkylene

polyamine and the molar ratio of alkyl substituted phenol, aldehyde and amine is between about 1:1:10 and about 10:0.1:10 and the amount of dispersant present ranges between 10 and about 75 parts by weight.

58. The additive composition of claim 43 wherein said nonvolatile fluidizer is selected from the group consisting of a lubricating mineral oil having a viscosity, at 100° F, of between about 500 and 2000 SUS, and a polyolefin oil having an average molecular weight between about 600 and about 3000.

59. The additive composition of claim 58 wherein said mineral oil is a refined naphthenic oil, said polyolefin oil is polypropylene or polybutene.

60. An additive concentrate comprising:

(a) an intake valve deposit controlling additive adapted for use in a spark-ignition internal combustion engine, said additive comprising between about 1 and about 30 parts by weight of, one or more primary amine carburetor detergents, between 1 and about 75 parts by weight of a dispersant selected from the group consisting of one or more polyalkylamines and Mannich bases, and between about 1 and 300 parts, by weight, of nonvolatile fluidizer oil per gallon of concentrate.

(b) the balance being a diluent suitable for combustion in said internal combustion engine selected from the group of consisting of hydrocarbons boiling in the range of between about 100° F and about 437° F and oxygen-containing hydrocarbons selected from methanol,

ethanol, propanol, methyl-tert-butyl ether, and ethylene glycol monobutyl ether.

61. The concentrate of claim 60 wherein said hydrocarbon is an aromatic hydrocarbon selected from toluene and xylene.

62. The concentrate of claim 60 wherein the concentration of said additive in said concentrate is between about 50 and about 4000 grams per gallon of concentrate.

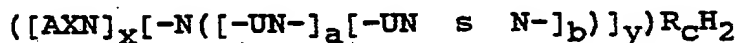
63. The concentrate of claim 60 further comprising between about 0.01 and about 0.2 weight percent of a dehazer.

64. The concentrate of claim 60 wherein said primary amines have the formula RNH_2 , wherein R is either (1) an alkyl or akenyl radical having from about 12 to about 22 carbon atoms or (2) a radical of the form $R-O-R'$ wherein R and R' are independently C_2 to C_{20} aliphatic radicals, hydrocarbyl radicals, alkyl radicals and alkenyl radicals, and the total number of carbon atoms in R and R' combined is between about 10 and about 30.

65. The concentrate of claim 60 wherein said primary primary amine is an alkyl or akenyl radical having from about 12 to about 18 carbon atoms.

66. The concentrate of claim 65 wherein said amine is oleyl amine, said amine being present in the range of 1 to about 30 parts by weight.

67. The concentrate of claim 60 wherein said fuel dispersant is a polyalkylamine having the following formula:



wherein s indicates the ring structure shown to be fully saturated, A is hydrogen, a hydrocarbon group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbon group having from 1 to about 10 carbon atoms, X is hydrogen, a hydrocarbon group having from 1 to about 10 carbon atoms or a hydroxyhydrocarbon group having from 1 to about 10 carbon atoms, with either of said groups being optionally taken with A to form a ring of from 5 to 6 annular members and up to about 12 carbon atoms total, U is an alkylene group of from 2 to about 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms, R is an aliphatic radical of from about 400 to about 5000 average molecular weight, a is an integer from 0 to 10, b is an integer from 0 to 1 with the sum of $a + 2b$ being an integer from 1 to 10, c is an integer of from 1 to 5 and equal to or less than the number of nitrogen atoms in the molecule, x and y are both 0 or 1, with the sum of x and y being equal to 1.

68. The concentrate of claim 67 wherein $y = 0$ and said dispersant is a polyalkyl monoamine selected from the group consisting of polypropyl amine, polyisobutyl amine, N-polyisobutyl dimethyl amine, N-polyisobutyl methylethylamine, N-polypropyl diethyl amine, N-polypropyl di(2-hydroxyethyl) amine, N-polyisobutyl N-methyl aniline, N-polyisobutyl morpholine, N-polyisobutyl piperidine, N-poly(1-butene) propylamine and N-polypropyl N-(2-hydroxyethyl) amine.

69. The concentrate of claim 68 wherein said monoamine has the general formula:



wherein R is a branched chain aliphatic radical, substantially free of olefinic unsaturation, of from about 40 to about 1250 average molecular weight and A is a lower alkyl having from 1 to about 3 carbon atoms.

70. The concentrate of claim 67 wherein $y = 1$, $x = 0$, U is $(CH_2)_d$, with d being 2 or 3, R is a branched hydrocarbon chain having from 2 to about 6 carbon atoms and having an average molecular weight in the range of 400 to 3000 and said dispersant is a polyalkyl polyamine.

71. The concentrate of claim 70 wherein said polyamine is selected from the group consisting of N-polyisobutyl ethylene diamine, N-polypropyldiamine, N-poly(1-butyl) ethylene diamine, N-(alternating copolymer of ethylene and isobutylene) ethylene diamine, N-polypropyl 2-aminoethylpiperazine, N-polyisobutyl 2-aminoethylpiperazine, N-polypropyl diethylene triamine,

N-polyisobutyl diethylene triamine, N-poly(1-pentyl) diethylene triamine, N-polypropyl trimethylene diamine, N-polyisobutyl trimethylene diamine, N-polypropyl di-(trimethylene) triamine, N-polyisobutyl di-(trimethylene) triamine, N-polyisobutyl 1,2-propylene diamine, N-polyisobutyl di-(1,2-propylene) triamine, N-polypropyl triethylene tetramine, N-polyisobutyl triethylene tetramine, N-(alternating copolymer of ethylene and isobutylene) triethylene tetramine, N-polypropyl tetraethylene pentamine, N-polyisobutyl tetraethylene pentamine and N-polyisobutyl pentaethylene hexamine.

72. The concentrate of claim 70 wherein said polyamine is a polyhydrocarbon radical substituted alkylene polyamine composition selected from the group consisting of N,N'-di(polypropyl) diethylene triamine, N,N'-di(polyisobutyl) diethylene triamine, N,N'-di(isobutyl) triethylene tetramine, N,N'-di(polypropyl) tetraethylene pentamine, N,N'-di(polyisobutyl) tetraethylene pentamine, N,N'N"-tri(polyisobutyl) tetraethylene pentamine, N,N'-di(polyisobutyl) 2-aminoethylpiperazine, N,N'-di(poly 1-butyl) triethylene tetramine and N,N'-di(polyisobutyl) di(trimethylene) triamine.

73. The concentrate of claim 70 wherein said polyamine is a straight chain polyamine having the following formula:



wherein a is an integer from 1 to 5, c is an integer

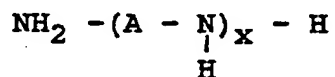
from 1 to 3, R is a polypropyl or polyisobutyl radical having an average molecular weight ranging from about 40 to about 3000, said amine having fewer R groups than nitrogen atoms.

74. The concentrate of claim 67 wherein said dispersant is present in a concentration between about 10 and about 75 parts by weight.

75. The concentrate of claim 60 wherein said dispersant is a Mannich base, said base being the condensation product of an alkyl substituted hydroxy substituted aromatic compound, an aldehyde and an amine with the alkyl substituent having an average molecular weight in the range between about 100 to about 100,000.

76. The concentrate of claim 75 wherein said alkyl substituent has an average molecular weight in the range between about 100 to about 5,000, the aldehyde is a low molecular weight aldehyde and the amine has at least one >NH group.

77. The concentrate of claim 76 wherein said hydroxy substituted aromatic compound is a polyalkyl phenol whose alkyl component is derived from 1-mono-olefinic polymers having an average molecular weight ranging between about 100 and about 3000, the aldehyde is formaldehyde and the amine is an alkylene polyamine of the formula:



wherein A is a divalent alkylene radical having from about 2 to about 6 carbon atoms and x is an integer ranging from 1 to about 10.

78. The concentrate of claim 77 wherein said polyalkyl phenol is selected from the group consisting of para substituted, mono-alkyl polypropylphenol and polybutylphenol, said amine is an alkylene polyamine and the mola ratio of alkyl substituted phenol, aldehyde and amine is between about 1:1:10 and about 10:0.1:10 and the amount of dispersant present ranges between 10 and about 75 parts by weight.

79. The concentrate of claim 60 wherein said nonvolatile fluidizer is selected from the group consisting of a lubricating mineral oil having a viscosity, at 100° F, of between about 500 and 2000 SUS, and a polyolefin oil having an average molecular weight between about 600 and 3000.

80. The concentrate of claim 60 wherein said mineral oil is a refined naphthenic oil and said polyolefin oil is polypropylene or polybutene, said fluidizer being present in a concentration of between 20 and 300 parts by weight.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/00973

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 10 L 1/14, C 10 L 1/22		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 10 L	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A, 0294045 (EXXON) 7 December 1988 see claims 1,15; page 4; page 9, lines 30-55; page 13; page 5, lines 1-31; page 1	1-3,13,14, 43-45,54, 55,60,61, 64,65,75, 76
Y	-- --	4-12,15-20, 22-41,46- 53,56-59, 63,66-74, 77-80
Y	FR, A, 1221034 (UNION OIL) 30 May 1960 see the whole document --	4,22-25,34, 35,46,66
Y	US, A, 3438757 (HONNEN et al.) 15 April 1969 see the whole document cited in the application --	5-12,17,18, 22-35,38, 39,47-53, 58,59,67- 74,79,80
./.		
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
1st June 1990	04.07.90	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	<i>H. Daniels</i> H. DANIELS	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	US, A, 4231759 (UDELHOFEN et al.) 4 November 1980 see the whole document cited in the application --	15-18, 22- 24, 34-39, 56-59, 77- 80
Y	US, A, 3849083 (DUBECK) 19 November 1974 see the whole document, particularly table 5 --	19, 20, 40, 41
Y	US, A, 3752657 (RICHARDSON) 14 August 1973 see the whole document --	63
A	US, A, 4022589 (ALQUIST et al.) 10 May 1977 see the whole document; particularly table I --	21, 42
A	US, A, 4116644 (JACKISCH) 26 September 1978 see the whole document -----	63

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9000973

SA 35034

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 27/06/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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FR-A- 1221034		None	
US-A- 3438757	15-04-69	DE-B- 1289355 FR-A- 1492000 GB-A- 1094020 US-A- 3565804 US-A- 3574576 US-A- 3844958 DE-A, B, C 1545487 FR-A- 1489559 GB-A- 1083610	12-06-75 23-02-71 13-04-71 29-10-74 02-07-70
US-A- 4231759	04-11-80	None	
US-A- 3849083	19-11-74	None	
US-A- 3752657	14-08-73	None	
US-A- 4022589	10-05-77	None	
US-A- 4116644	26-09-78	None	

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